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DESCRIPTION

[0001] The present invention relates to the field of an architectural concrete and a dry premix, having improved property to maintain, after the installation, for longer time periods the brilliance and the colour quantity.

PRIOR ART

[0002] One of the most important use for cement (either grey or white) is in the manufacture of the so called "architectural concretes", i.e. castings in work with not treated (flat or profiled) or treated (for example sand-blasted) surfaces. Particularly the white cement is used as a decorative element in the light prefabrication and in the production of paving tiles. The architectural concrete composition, particularly the white one, must meet the requirement to obtain besides good mechanical resistances and durability with time also surfaces having good appearance and therefore uniform in colour and texture.

[0003] In order to obtain architectural concretes having homogeneous colour and constant composition it is essential the selection of the inert material but, while said inert material forms up to 80% of the concrete mass, the concrete surface has a composition differing from the underlying layers and therefore from its whole mass:
the coarse inert material does not appear on the surface and the surface itself consists only of cement paste and sand.

[0004] As a consequence a surface of concrete manufactured with white cement and light sand turns out to be good, even if the coarse aggregate is darker.

[0005] The colour uniformity of the sand is less important than in the case of grey cement architectural concrete: the colour constancy of the white cement may cover, obviously within certain limits, the colour variations of the sand.

TECHNICAL PROBLEM

[0006] The principal problem of architectural concrete manufactures, both in grey cement and in white cement, concerns the constant maintenance with time of the original appearance; it is important to defer as late as possible the natural ageing process due, essentially, to the influence of atmospheric agents.

[0007] The protection of these manufactures is principally carried out with water-repellent products which are applied on the surfaces by spray or brush, as for example silicone solutions, which are stable in an alkaline environment, and possibly to light and bad weather.

[0008] However, perhaps owing to the progressive increase of pollutants present in a typical metropolitan environment, the superficial protection of these products resists in towns for a more and more limited time with subsequent aesthetic degradation of the manufacture. In most cases the quick aesthetic degradation of these materials prevents from using these architectural concretes.

[0009] Therefore the need is felt to solve the problem of the preservation of the original appearance of the surface of the architectural concretes for longer time periods.

SUMMARY OF THE INVENTION

[0010] The Applicant has surprisingly found that this problem may be effectively solved by the use according to claim 1.

[0011] The photocatalyst able to oxidize in the presence of light, air and environmental humidity (oxygen and water) the polluting substances contacting the surface of the hydraulic binder (or the relative mortars and concretes) in a hardened state, being part of the present invention, is a titanium dioxide, mainly in the form of anatase, or a precursor thereof, optionally doped with other atoms different from Ti.

DETAILED DESCRIPTION OF THE FIGURES

[0012]

Figures 1-4 report the images of the surfaces relating to the compositions of cement mortars D, E, F, G reported in Example 2.

In particular Figures 1A - 1B report the surface images relating to composition D, Figures 2A - 2B to composition E, Figures 3A - 3B to composition F, Figures 4A - 4B to composition G.

Figure 5 represent the % reflectance (R%) for the sample B encompassed in Example 5 measured at different times as a function of the wavelength (in nm).

Figure 6 represent residual Q% as a function of time of samples (A) •, (B)
▲
, (C)
■
, described in Example 5 subjected to a wavelength higher than 290 nm (450 nm).

Figure 7 represents hystograms of residual Q% of the white cement treated with 5% P-25 ® and white cement not treated (as such).

DETAILED DESCRIPTION OF THE INVENTION

[0013] In the present description for "binder" or "hydraulic binder" we mean a hydraulic cement material, in powder form at the solid state, dry, which, once mixed with water, provides plastic mixtures able to set and harden. In the wide definition of "hydraulic binder", according to the present invention, are included both (white, grey or pigmented) cements as defined according to UNI ENV 197.1 standard and the so called cements for debris dams, cement agglomerates and hydraulic limes, as defined in the 1965, May 26 No. 595 Law. The present invention does not only regard the hydraulic binder wherein the photocatalyst is added to one of its components such as clinker or gypsum, in any phase of the relative preparation, but also a dry premix, namely a material comprising any hydraulic binder to which, before the installation thereof, photocatalyst particles are added.

[0014] An object of the present invention is the use of an architectural concrete cement composition comprising the photocatalyst.

[0015] By "dry premix" we mean a homogeneous mixture of binder and aggregate and optionally at least one additive suitable to be mixed with water and for the preparation of concretes.

[0016] By "cement composition" or "cement mix" we mean any composition in which a binder is mixed with water, and with aggregates having different granulometry.

[0017] The "aggregates" or "inert materials" may be coarse aggregates, such as crushed stones or pebble gravel, or fine aggregates, such as sand, and they are classified in the UNI 8520 standard.

[0018] The "clinker" used for the preparation of the binder is any clinker of Portland cement as defined according to the UNI ENV 197.1 standard, i.e. a hydraulic material consisting of at least two thirds in mass of calcium silicates (3CaO SiO_2) and (2CaO SiO_2), the remaining part being Al_2O_3, Fe_2O_3 and other oxides.

[0019] The hydraulic binder, the dry premix or the cement compositions may then contain white, grey or pigmented cement, preferably white cement.

[0020] The particular property distinguishing essentially the white cement from the other cements is just that it is perfectly white.

[0021] Grey colouring of common Portland cements derives from the presence of iron and other metal compounds.

[0022] White cement is obtained from raw materials which at the pure state are perfectly white and "white" pigmentation is the demonstration of the purity of its composition.

[0023] The dry premixes preferably contain white cement and they are characterized in that they maintain after their installation for longer time periods the brilliance and the colour quantity.

[0024] The present invention further relates to the use of a photocatalyst added "in bulk" to a hydraulic binder or to an agglomerate in order to preserve with time the aesthetic appearance, the brilliance and the colouring quantity.

[0025] In the present description the word in bulk means that the photocatalyst is added to the mass of the binder, and then it is distributed in the whole mass, that is even in the inner and deeper layers, and not only on the,surface of the present binder, and consequently also of the mix or the premix obtained therefrom.

[0026] As far as dry premix is concerned, the definition "in bulk" means that photocatalyst particles are homogeneously mixed with the various components of said premix. In other words the dry premix may comprise both the binder already containing the photocatalyst and separately a conventional hydraulic binder and particles of photocatalyst.

[0027] The photocatalyst used according to claim 1 is titanium dioxide or one of its precursors,

[0028] The photocatalyst particles present in the hydraulic binder of the present invention are particles of titanium dioxide (TiO_2) having anatase structure for at least 5%, preferably for 25%, more preferably at least 50%, even more preferably for at least 70% by weight. In a preferred aspect of the invention the TiO_2 P-25®, commercialized by Degussa, which is a mixture 70:30 of anatase TiO_2: rutile TiO_2, has been used.

[0029] In fact it is known that TiO_2 crystallizes into the tetragonal forms of anatase and rutile. The rutile is the most stable and industrially most important form.

[0030] The anatase may turn into rutile also at room temperature but with an extremely low velocity.

[0031] At higher temperatures the transformation velocity is more significant. The transformation from rutile to anatase is instead impossible for TiO_2 crystals; industrially this transformation is made possible thanks to the orienting action of certain impurities although the same are present in minimal quantities.

[0032] The expression "titanium dioxide precursor" means that the preferred photocatalyst is not only limited to "TiO_2 prevailingly in the form of anatase" but it is extended also to any product which added to the baked clinker, to the hydraulic binder, to the premix or to the mix, may form the TiO_2 mainly under the anatase form optionally by suitable thermal treatments.

[0033] For example the so called "titanium paste" may be considered a valid precursor for the titanium dioxide based photocatalyst of the present invention.

[0034] The titanium paste ($TiO_2 \cdot H_2O$) derives from the treatment of the product $TiOSO_4$ with water and it may be effectively used as an anatase precursor without a particular thermal treatment. A particularly effective titanium paste is commercialized by TIOXIDE®.

[0035] The photocatalytic activity may also be obtained on TiO_2 matrices doped with suitable atoms such as Fe(III), Mo(V), Ru(III), Os (III), Re(V), V(IV) and Rh(III).

[0036] Particularly these atoms may substitute, at the atomic level, the Ti(IV) present in the TiO_2 matrix for at least 0.5%.

[0037] The method for obtaining such photocatalysts is described in literature for example in J. Phys. Chem. 1994, 98, 1127-34, Angew. Chemie 1994, 1148-9 and in Angew. Chemie Int., Ed. 1994, 33. 1091.

[0038] The quantity of photocatalyst present in the hydraulic binder or in the mix is ranging from 0,01 to 10% in bulk calculated with respect to the binder Therefore even extremely low percentages of photocatalysts may produce a very high effect of colour conservation with time.

[0039] By "environmental polluting substances" we mean the organic substances which may be present in the environment due to cars exhausts or industrial waste such as benzene, volatile aromatic compounds, pesticides, organic aromatic compounds,

benzofluorides, etc.

[0040] According to a particularly preferred aspect of the present invention phenanthroquinone has been used as the organic polluting substance. The selection of this specific compound is considered particularly significant to demonstrate the great advantage obtainable with the products object of the present invention.

[0041] In particular this selection was made on the basis of the preliminary knowledge of the more or less significant percentage components of a typical environment of big towns.

[0042] An important class of compounds present as pollutants in the troposphere is that of polycyclic aromatic hydrocarbons (PAH). These compounds and their analogues containing the heteroatoms (such as S, N, 0), derive from the incomplete combustion of organic material such as carbon, oil, wood, fuels, etc. The PAH mechanism formation is based on the production of free radicals by hydrolysis (~500+800°C) of hydrocarbons in the reducing zone of the flame, characterized by having an insufficient oxygen flow, the structure of these compounds is characterized by containing at least two condensed aromatic rings in the same molecule.

[0043] As it was demonstrated in several experiments in vitro and in vivo, many compounds belonging to said class show mutagen and carcinogen activity. In particular, phenanthroquinone belonging to PAH class was selected for the following reasons:

- it is a substance not raising handling problems;
- it is a substance giving a yellow colouring and its disappearance may be followed visually;
- it is soluble in methanol, a solvent easly evaporating, once it is applied onto the surface to be treated.

[0044] Neither inorganic pollutants are to be excluded such as the nitrogen oxides NO_x which with the photocatalyst according to the present invention can be oxidized to nitrates.

[0045] The photocatalytic action of titanium dioxide is well known in the art, as it is known that TiO_2 particles may adhere to inorganic substrates such as cement.

[0046] On the contrary what is not described is the use of titanium or, more generally, of a photocatalyst, in bulk, in the cement or in the mix in order to maintain constant the quality of the superficial appearance in terms of brilliance and colour quantity of the hardened manufacture. By "colour quantity" we mean the ensemble of the characteristics of dominating wavelength and purity, as defined below. Thanks to the peculiar aspect to maintain with time unaltered the colouring, a preferred aspect of the invention relates particularly to the use of white cement and prepared cement as hydraulic binder.

[0047] The "white colouring" of the cement may be characterized by three properties:

as brilliance, that is power to reflect the incident light (which is the typical characteristic of white bodies in contrast to black bodies), expressed as per cent ratio between the light reflected by a surface of white cement and the one reflected by an equal surface of magnesium oxide, conventionally considered the ideal white body; in white cements produced in Italy the brilliance value is higher than 82, and in mortars produced with these cements it is a little lower;

as dominating wavelength, that is tonality of the gradation which accompanies and characterizes every white (in fact white bodies are not equal among each other); the dominating wavelength lies between yellow and blue;

as purity, or intensity of the gradation; purity is measured by the percentage of colour, which is lower than 5%.

[0048] The use of photocatalysts therefore allows to keep constant as long as possible these three important properties.

[0049] White cement may also be pigmented in order to obtain an additional chromatic effect.

[0050] This effect turns out to be decidedly better than the one obtainable, at equal conditions, with grey cement. It is interesting to notice that white cement, owing to its chemical composition, does not affect either the tone or the luminosity of the colouring obtained with the pigment (alterations which on the contrary are unavoidable with the use of the grey cement).

[0051] The pigment is to be mixed intimately in the mixture or, separately, with the cement. The percentage of addition is to be searched case by case according to the chromatic effect which one wish to obtain. This percentage is referred to the weight of the cement (e.g., if mineral pigments based on iron oxide are used, the above mentioned percentage is about 2% with respect to the weight of the cement).

[0052] Pigments are generally: inorganic base dyes as for example natural dyes (yellow ocher, reds based on iron oxide such as red ocher, English red, Spanish red; amber earth colour; ultramarine blue; etc.) or mineral dyes (yellow zinc chromate; Schweinfurt green; Berlin blue; Bremen blue); lead based dyes such as Naples yellow; chrome yellow; the group of mineral dyes based on iron oxide (having a chromatic range from brown to orange and to yellow).

[0053] As it has been previously described with the binder architectural concretes can be produced preferably manufactured with premixes comprising white cement and characterized by maintaining for longer time periods the brilliance and the colouring quantity.

[0054] Concretes manufactured with the binder have binders/aggregates ratios by weight ranging from 1/3 to 1/6.

[0055] The water quantity used in the cement compositions is that sufficient to complete the hydration reaction of the binder and to provide the optimal workability at the plastic state of the mixture. The proportion among water, binder and possible aggregates of the cement compositions may vary within wide limits, and it is a function of the properties and the final uses of the desired mortars and concretes. In general terms the water quantity ranges from about 20 to 60% by weight with respect to the weight of the binder.

[0056] The method for preparing mix may be any conventional one. The temperature of mix formation between the binder and water, and aggregates, generally ranges from +5° to 30 °C, and it is preferably at least 20 °C.

[0057] The photocatalyst addition to the hydraulic binder is not a critical phase; the photocatalyst may be simply added to the powder of the hydraulic binder and mixed according to any technique known in the art, by using both an automatic mixer and manually.

[0058] Being the simple addition of the photocatalyst to the binder in powder form possible, the premixes are preferred. We report hereinbelow the following Examples of the invention for illustrative but not limitative purposes. It is necessary to point out that an exhaustive exemplification of the invention can be carried out only by very long (of the order of years) procedures because the correct evaluation of the maintenance of the characteristics of the hardened binders, particularly of architectural concretes, need natural "ageing" procedures in the real microclimate.

Embodiment 1

[0059] The following embodiments are useful for understanding the invention.

[0060] Some supports having 25 x 8 x 2.5 cm size have been realized with normal cement mortar based on Italbianco Italcementi 52.5® white cement.

[0061] After manufacturing the test samples have been cured for 1 day in the molds in the environment at 20 °C and RH > 90%; after ejection they have been stored for further 7 days at 20 °C and RH = 60% (RH = Relative Humidity).

[0062] These test samples have then been used as supports for the applications of a cement mortar added with titanium dioxide. The base mortar had the following formulation:

Italbianco Italcementi white cement	35.4%
Metakaolin	3.5%
Quartz (0.06-0.25 mm)	59.7%
Cellulose Ether	0.2%
MELMENT F10 (melanine condensed with formaldehyde)	0.25%
Cellulose Fibres	0.25%

ELOTEX 50 AV/90 Terpolymer (butylacrylate/vinylacetate/vinyl versatate) terpolymer	0.7%
Ratio Water/Cement	0.60

[0063] In particular, six compositions have been realized using the following dosages of titanium dioxide, referred to the weight of the cement:

0 - as such (titanium dioxide 0%)

1 - 10%

2 - 5%

3 - 1%

4 - 0.5%

5 - 0.1%

[0064] Titanium dioxide, commercialized under the P-25 trade-mark of Degussa, has been used.

[0065] Every composition has been vigorously stirred for 5 minutes by means of a high speed mixer, until obtaining of a fluid consistency (spatulable).

[0066] Subsequently, the compositions have been applied with a metallic spatula on the above described supports; at the end of the application the average thickness of the mortar turned out to be of about 2 mm.

[0067] The test samples, so realized, have been then cured for 7 days at 20 °C and RH = 60%. Then 0.5% alcoholic solution of various condensates based on polycondensated aromatic compounds has been applied with a brush onto half surface of each test sample (about 100 cm^2). 6 g, (corresponding to 0.03 g of dry product) of this solution, having a yellow coloration, have been applied on every 100 cm^2 as a consequence that 0.3 mg/cm^2 have been applied on each sample.

[0068] Every test sample showed at the end of the treatment two zones with well distinct colourings:

yellow, the treated part

white, the untreated part.

[0069] Then the test samples thus treated have been submitted to image analysis with a LEICA Quantiment 500+ computerized analyzer to detect white tonalities.

[0070] Subsequently, they have been exposed, at a distance of about 50 cm, to a 300 Watt OSRAM Ultra-Vitalux lamp having a mixture of radiations similar to the high mountains natural solar radiation (Ultraviolet + visible).

[0071] At time intervals of 8, 16, 24 and 60 hours of exposure, the image analyses have been repeated to detect white tonalities. The obtained results have been reported in Table 1.

TABLE 1

	WHITE VALUES						
Time (h)	Not treated specimen	TiO2 free specimen	1	2	3	4	5
0	211	183.2	185.4	184.5	183.7	184.7	182.7
8	211	185.3	200.1	194.9	190.5	189.5	188.1
16	211	187.1	203.5	197.6	194.1	192.6	191.1
24	211	190.0	206.2	200.8	197.7	195.6	193.2

	WHITE VALUES						
Time (h)	Not treated specimen	TiO2 free specimen	1	2	3	4	5
60	212	194.9	211.9	206.5	204.5	203.6	201.0

[0072] As it results the test samples containing 10% of titanium dioxide, after 60 hours of exposure, show the same tone of white of the untreated surfaces; it must be pointed out that already after 8-16 hours of exposure white tonalities result to be very close to the not treated surfaces.

[0073] The test pieces containing the lowest dosages of titanium dioxide show an analogous trend, but obviously at lower levels, however proportional to the titanium dioxide content.

[0074] It may be observed that a certain bleaching action through the effect of light is obtained also on the test sample without TiO_2. In any case, low quantities of TiO_2 are sufficient to obtain a much greater bleaching effect.

[0075] However, from the visual observation of what has been instrumentally measured it results a more marked bleaching of the treated surfaces, especially if moistened, if compared to the not-treated surface.

EMBODIMENT 2

[0076] 4 cement mortar compositions (of identical formulation as those of Example 1) added with TiO_2 (P-25®- Degussa) have been manufactured following substantially the procedure described in the Example 1. In particular:

Composition	D - 5% of titanium dioxide by weight
	E - 1% " "
	F - 0.5% " "
	G - 0.1% " "

[0077] Unlike Example 1 the cement compositions have been applied to an external plastered wall of a building.

[0078] Every composition has been applied onto a surface of about 600 cm^2; the average thickness turned out to be equal to 1-2 mm.

[0079] Half of every surface (300 cm^2), corresponding to every composition above reported, has been treated with the same alcoholic solution comprising the organic pollutants of Example 1 (0.2 mg/cm^2 of dry product); then 2 surfaces have been obtained having well distinct colorations: yellow the treated part, white the not treated part.

[0080] In Figures from 1 to 4 the images relative to the four compositions have been reported, in particular: Figure 1A - 1B: composition D;

[0081] Figure 2A - 2B: composition E; Figure 3A - 3B: composition F; Figure 4A - 4B: composition G. The Figures 1A, 2A, 3A and 4A refer to the images of the surfaces relative to the four compositions D, E, F and G respectively immediately after the treatment with an alcoholic solution of half of said surfaces, the part coloured in yellow being indicated in every Figure with the T letter. After 1 week of exposure to sunlight the compositions have been photographed again and their images are reported in Figures 1B, 2B, 3B and 4B, which refer to the four compositions D, E, F and G respectively after 1 week exposure.

[0082] As it results from Fig. 1B - 4B the surfaces treated with the organic pollutant reported to the original white.

EMBODIMENT 3

[0083] Tioxide titanium paste (TiO_2 precursor) has been added at concentrations of 0.1%, 1% and 5% by weight respectively to

the cement whose chemical and spectrometric analysis is reported in Table 2.

TABLE 2

Chemical Analysis	
Ignition Loss	2.68%
Brilliance	90.0
Dominating Wavelength	569 nm
Purity	2.3%
F	0.380%
X Rays Spectrometric Analysis	
SiO_2	21.80%
Al_2O_3	3.60%
Fe_2O_3 CaO	0.25%
CaO	65.86%
MgO	0.98%
SO_3	3.15%
Na_2O	0.83%
K_2O	0.10%
SrO	0.08%
Mn_2O_3	<0.04%
P_2O_5	0.09%
TiO_2	0.03%

[0084] With every mixture 3 test samples having 40 x 40 x 160 mm size have then been prepared in normal mortar according to EN 196.1 standard (cement/sand = 1/3, w/c ratio = 0.5).

[0085] By comparison 3 test samples without addition of titanium paste have been prepared.

[0086] The twelve test samples have been stored in a humid environment for 24 hours and once ejected they have been stored immersed in water up to the expiry of 28 days.

[0087] Then compressive strength tests have been carried out whose average results are reported in Table 3.

TABLE 3

	1	2	3	4
Titanium paste content (%)	-	0.1	1	5
Comprensive strength (MPa)	58.1	58.2	57.4	56.7

[0088] As it results the addition of a TiO_2 precursor does not affect significantly cement compressive strength.

Embodiment 4

[0089] 4 mortars with Italbianco Italcementi 52.5® cement having compositions (by weight) reported in Table 4 have been manufactured.

TABLE 4

	A	B	C	D
Italbianco® Cement	450	450	450	450

	A	B	C	D
White Aggregate (0.1-2 mm)-g	1350	1350	1350	1350
TiO2 P-25®-g	-	0.45	0.90	4.5
(% by weight of cement)	-	(0.1%)	(0.2%)	(1%)
Water	225	225	225	225

[0090] With every mortar 3 test samples having 8 x 8 x 2 cm size have been manufactured. The test samples have been cured for 1 day in molds in an environment at 20 °C and R.H. >90%, after ejection they have been stored for further 7 days at 20 °C at R.H. about 60%. The twelve test samples have been submitted to a colorimetric test with a Cologard System 0.5 colorimeter in order to estimate brilliance, dominating wavelength and purity of the casting surface (8 x 8 cm). The results are reported in Table 5.

TABLE 5

Paving tile No.		Brilliance	Dom. Wavelength	Purity
As such	1	82.3	576	3.9
	2	81.4	576	3.9
	3	81.9	576	3.9
TiO2 0.1%	4	81.6	576	3.9
	5	80.6	576	3.5
	6	80.7	576	3.5
TiO2 0.2%	7	81.1	576	3.5
	8	79.8	576	3.5
	9	80.3	576	3.5
TiO2 1%	10	81.3	576	3.5
	11	81.5	576	3.5
	12	81.2	576	3.5

[0091] Then the test samples have been exposed in an external environment subject to strong car traffic for 6 months. After this period the above described colorimetric measures have been repeated. The results are reported in Table 6.

TABLE 6

Paving tile No.		Brilliance	Dom. Wavelength	Purity
As such	1	80	578	4.3
	2	79.5	578	4.4
	3	79	579	4.3
TiO2 0.1%	4	80	576	4.0
	5	80	576	3.6
	6	80	576	3.5
TiO2 0.2%	7	80.5	576	3.6
	8	80.5	576	3.5
	9	80.5	575	3.5
TiO2 1%	10	82	575	3.2
	11	82	575	3.3
	12	81.5	575	3.2

[0092] As it results brilliance, dominating wavelength and purity values of the test samples with titanium dioxide undergo with time lower changes if compared to the values of the test samples of the cement as such (without TiO_2).

Embodiment 5

[0093] 2 samples of white cement (2 mm thick) are prepared on suitable supports having a discoid form with a diameter of 3.2 cm and thickness of 7 mm (substantially as described in Example 1).

[0094] 2 samples containing 5% TiO_2 respectively of P-25®Degussa type (sample A) and AHR®(Tioxide) type (sample B).

[0095] For comparison purposes a third sample (C) without TiO_2 is prepared. In order to obtain surface reproducible and constant amounts of organic substance on the sample a phenanthroquinone solution in methanol is deposited by means of an aerograph thereby giving to a surface phenanthroquinone concentration equal to 0.1 mg of dry product/cm^2. At the end of said treatment every sample showed a homogenous surface of yellow colour.

[0096] Both before and after the deposition of the organic substances, reflectance spectrophotometric analyses have been carried out with a Perkin Elmer lambda 6 type spectrophotometer provided with an integrating sphere to eliminate scattered light responsible for anisotropy and surface irregularities.

[0097] The samples have been irradiated by means of a solar flow simulator, emitting radiation with wavelength higher than 290 nm.

[0098] The device used for irradiating consists of four 400 Watt lamps placed at the vertices of a square having at the center a carrying sample roundabout rotating on its own axis. By means of said device it has been possible to irradiate contemporaneously more samples with the same amount of photons per time unit.

[0099] The irradiation device SOLAR SIMULATOR SET-UP12/24 allows to carry out accelerating ageing test, wherein approximately 100 irradiation hours correspond to 1 year of sunlight.

[0100] For every sample at different times various % reflectance (R%) as a function of wavelength (nm) have been obtained.

[0101] The reflectance as previously pointed out is obtained by the ratio reflected light on a surface/inciding light on said surface.

[0102] The % reflectance of the sample B are reported in Figure 5 at different time as a function of wavelength (nm).

[0103] In particular with respect to Figure 5, the curve 1 represents the spectrum before depositing the organic substance, the curve 2 represents the situation after deposition of said substance, the curves 3, 4, 5 represent the situation respectively after 2, 4 and 8 hours of irradiation. As it results already after 8 hours of irradiations the situation is almost the same as before the treatment with the pollutant.

[0104] The reflectance values must be normalized to allow a comparison among different materials having therefore a difference intrinsic reflectance.

[0105] The normalization coefficient Nt is defined as follows:

$$Nt = [Rt_o - R_t]/Rt_o$$

wherein Rt_o is the reflectance of the sample at the time = 0, before the application of the polluting substance, R_t is the reflectance at the time t after the addition of the polluting substance (in this case the phenanthroquinone).

[0106] The normalization coefficient thus determined allows to calculate the residual Q% rendering possible a comparison among different material having a different intrinsic reflectance. In fact residual Q% may be easily calculated by applying the following the mathematical formula

$$\text{residual } Q\% = \frac{1 - Nt_o poll - N_t}{Nt_o poll} \cdot 100$$

wherein Nt_opoll is the normalization coefficient of the material after addition of the pollutant at t = 0.

[0107] In table 7, residual Q% is reported as a function of the time of the above mentioned samples (A) (containing 5% P-25), (B)

(containing 5% AHR®) and (C) (the sample without TiO_2) subjected to a wavelength higher than 290 nm (450 nm) and an air flow at T=60°C.

TABLE 7

Time (hours)	P-25® residual Q% (A)	AHR® residual Q% (B)	as such residual Q% (C)
0	100	100	100
1	68.6	78.4	85.4
2	56.2	64.9	75.6
3	46.9	51.4	61.0
4	37.5	43.3	53.7
5	-	-	-
6	20.9	20.3	41.5
8	9.0	11.4	29.7

disappearance of yellow colour

yellow tones

[0108] As it results from Table 7, samples containing titanium oxide give with time lower and lower normalized values, index of the photocatalyst activity.

[0109] The analytical data are also confirmed visually. In fact the total disappearance of yellow colouring due to phenanthroquinone is observed in samples containing TiO_2.

[0110] Although the normalized values corresponding to sample C decrease with time, visually it is possible to observe definite yellow zones on the sample surface.

[0111] As it again results from Table 7 the process works with different types of titanium oxide, prevailingly in the anatase form.

[0112] Figure 6 resumes in the form of a diagram wherein residual Q% is reported in ordinates and time (hours) is reported in abscissae, the data of table 7.

Embodiment 6

[0113] Using substantially the same process and the same device as those of Example 5, the photocatalytic activity of titanium dioxide P-25® on a white cement sample (prepared as described in Example 5) onto which carbon black was deposited.

[0114] Carbon black was deposited according to the following technique: a white cement discoid treated with 5% TiO_2 P-25® (Degussa) has been left for 10 minutes at a height of 10 mm from the flame of a candle. For comparison purposes the same test has been conducted on a sample without TiO_2.

[0115] The results of said tests are reported in Figure 7.

[0116] As it results from histograms of Figure 8 the activity of the sample containing TiO_2 is evident.

Embodiment 7

[0117] The nitrogen oxides, comprising both NO and NO_2 (generally indicated with NO_x) play an important role in the atmoshpere chemistry.

[0118] A high concentration of these oxides with respect to the average quantity of the same in a not polluted area is due to the presence of movable sources (vehicles) and stationary sources and can originate acid rains or organic compounds such as

peroxyacetyl nitrates (PAN) being irritating for eyes and phytoxic from plants.

[0119] Following substantially the technique described in Example 1, a white cement sample containing 1% by weight of TiO_2 of the AHR®type was prepared.

[0120] The cement plate thus obtained has been placed at the base of a Plexyglass® glass box of 1 l capacity to evaluate the efficiency of NO_x remotion from the cement containing the photocatalyst.

[0121] An air flow has been passed containing 0.6 ppm NO_2, 0.5 ppm NO and 60% relative humidity through the above described box lightened from the top by three 300 Watt Hg vapour lamps (emitting light with wavelength higher than 360 nm) placed at a distance of 15 cm from the sample.

[0122] The air flow of 2 l/min has been divided to guarantee a sufficient contact time of the air with cement, and to have a suitable flow for the detection system working Monitor cabs 8440 NITROGENOXIDE ANALYZER®chemiluminescence detector.

[0123] For comparison purposes the same technique has been carried out on a cement sample not containing TiO_2.

[0124] The NOx decrease measured in the air leaving the box containing the cement sample with TiO_2 is of about 40% already after 3 hours of air flow, whereas no significant NOx reduction is observed in the air leaving the box containing the cement sample without TiO_2.

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- J. Phys. Chem., 1994, vol. 98, 1127-34 [0037]
- Angew. Chemie, 1994, 1148-9 [0037]
- Angew. Chemie Int., 1994, vol. 33, 1091- [0037]

Patentkrav

1. Anvendelse af en bygningsbetonkomposition, indeholdende i bulk fotokatalysatorpartikler, som er i stand til at oxidere forureningssubstanser i nærvær af lys, luft og omgivelsesfugtighed, idet nævnte komposition omfatter vand, grove og fine aggregater, et hydraulisk bindemiddel og fotokatalysatorpartikler, og som har et vægtforhold mellem bindemidler/aggregater i området fra 1/3 til 1/6, hvor fotokatalysatorpartiklerne er partikler af titaniumdioxid, mindst 5 vægt% af nævnte partikler af titaniumdioxid har anatase strukturen, nævnte fotokatalysatorpartikler er til stede i en mængde i området fra 0,01 til 10,0 vægt% med hensyn til det hydrauliske bindemiddel.

2. Anvendelse ifølge krav 1, hvor mindst 25 vægt% af nævnte partikler af titaniumdioxid har anatase strukturen.

3. Anvendelse ifølge krav 2, hvor mindst 50 vægt% af nævnte partikler af titaniumdioxid har anatase strukturen.

4. Anvendelse ifølge krav 2, hvor mindst 70 vægt% af nævnte partikler af titaniumdioxid har anatase strukturen.

5. Anvendelse ifølge krav 1, hvor titaniumdioxidet er en blanding 70:30 af anatase TiO_2 : rutil TiO_2.

6. Anvendelse ifølge krav 1, hvor en precursor af titaniumdioxid er en titanium pasta.

7. Anvendelse ifølge krav 1, hvor de fotokatalytiske partikler er partikler af titaniumdioxid dopet med et eller flere atomer, som er forskellige fra titaniumatomer.

8. Anvendelse ifølge krav 7, hvor atomerne, som er forskellige fra titaniumatomer, er valgt fra gruppen bestående af Fe(III), Mo(V), Ru(III), Os(III), Re(V), V(V) og Rh(III).

9. Anvendelse ifølge krav 1, hvor fotokatalysatoren er til stede i en mængde lig 0,1 vægt% med hensyn til bindemidlet.

10. Anvendelse ifølge krav 1, hvor det hydrauliske bindemiddel er valgt fra en gruppe bestående af et hydraulisk materiale bestående af mindst to tredjedele på massebasis af calcium silicater ($3CaO\ SiO_2$) og ($2CaO\ SiO_2$), og en tredjedel er Al_2O_3, Fe_2O_3 og andre oxider, et cementbindemiddel og et hydraulisk kalk.

11. Anvendelse ifølge krav 1, hvor bygningsbetonkompositionen er fremstillet af et tørt premix indeholdende grove og fine aggregater, et hydraulisk bindemiddel og fotokatalysatorpartikler, og som har et vægtforhold mellem mindemidler/aggregater i området fra 1/3 til 1/6, hvor fotokatalysatorpartiklerne er partikler af titaniumdioxid, mindst 5 vægt% af nævnte partikler af titaniumdioxid har anatase strukturen, nævnte fotokatalysatorpartikler er til stede i en mængde fra 0,01 til 10,0 vægt% med hensyn til det hydrauliske bindemiddel.

DRAWINGS

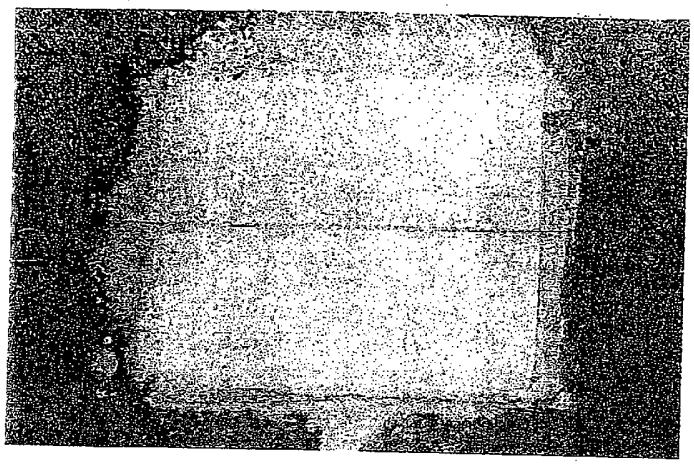


FIG. 1B

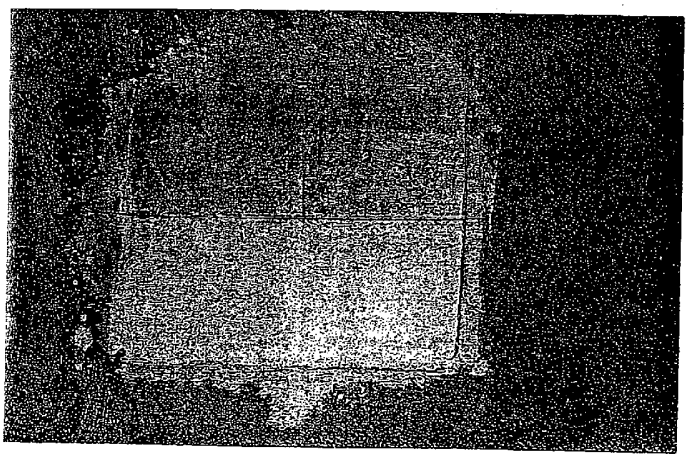


FIG. 1A

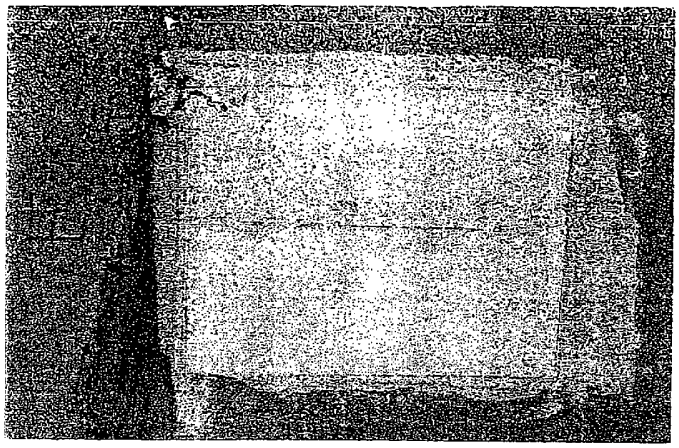


FIG. 2B

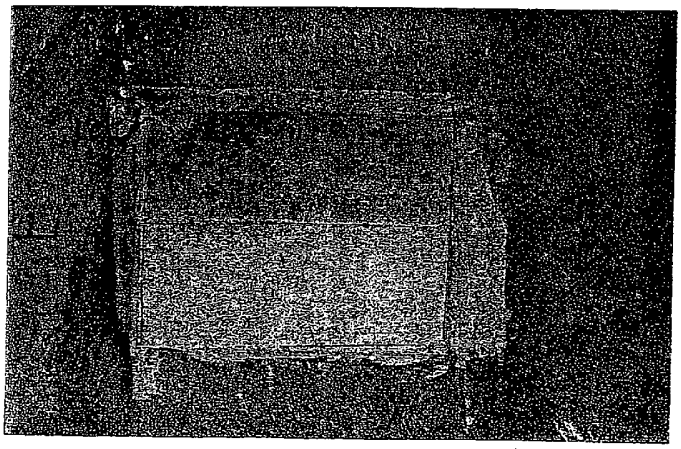


FIG. 2A

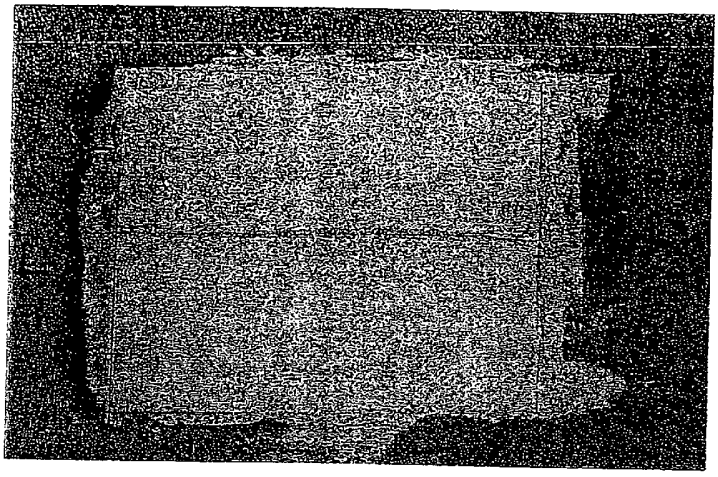


FIG. 3B

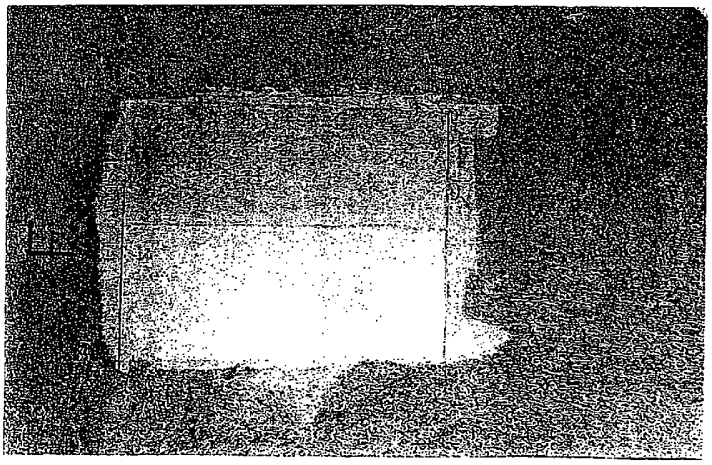


FIG. 3A

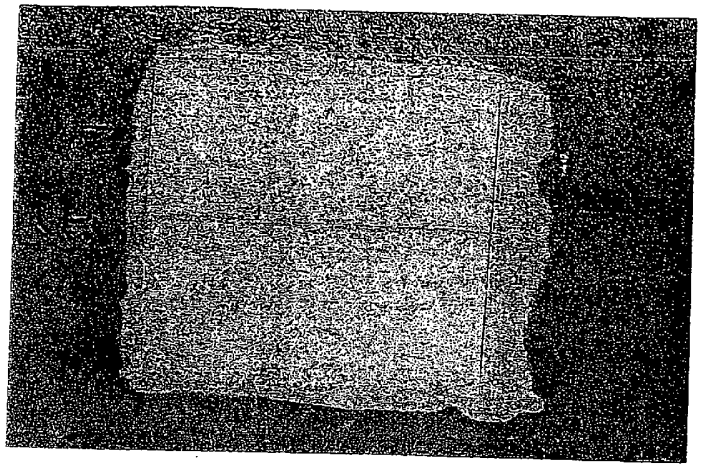


FIG. 4B

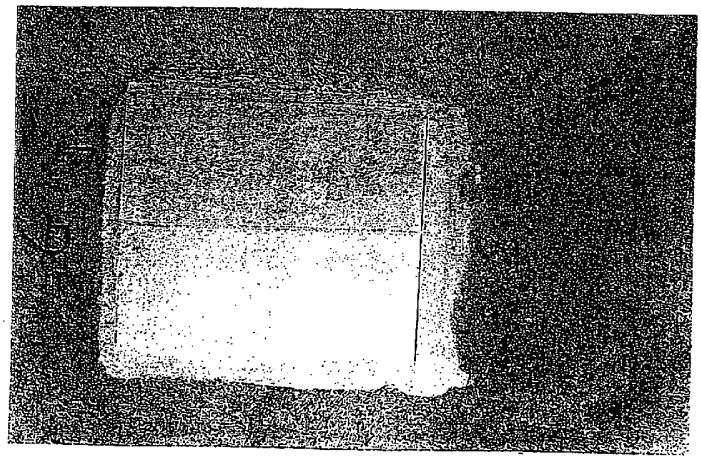


FIG. 4A

Fig.5

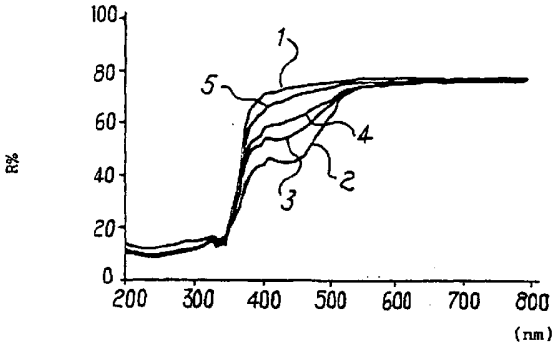

R%
100
80
60
40
20
0
200
300
400
500
600
700
800
(nm)
1
2
3
4
5

Fig.6

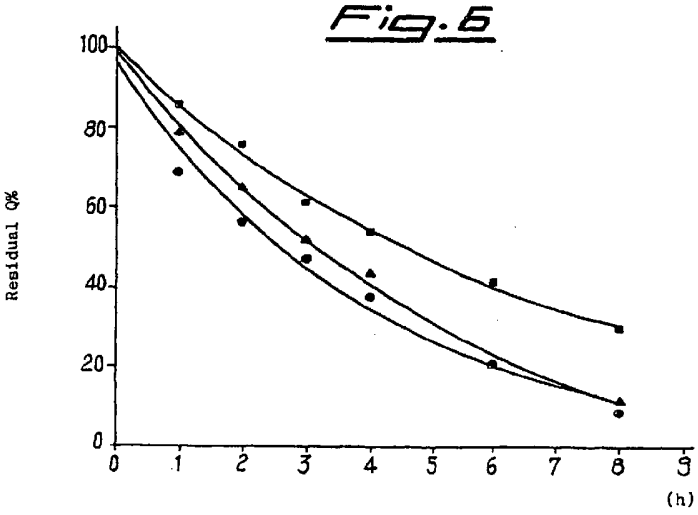

Residual Q%
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
(h)

Fig.7

